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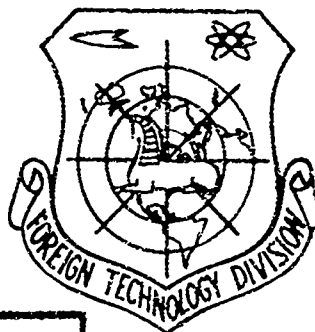
## FOREIGN TECHNOLOGY DIVISION



### COMPUTATION OF THE VIBRATIONAL FREQUENCIES OF A MOLECULE OF HYDRAZIN $N_2H_4$

By

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COMPUTATION OF THE VIBRATIONAL FREQUENCIES  
OF A MOLECULE OF HYDRAZINE  $N_2H_4$

Yu. I. Kotov, G. S. Koptev, and V. M. Tatevskiy

To the investigation of the vibrational spectrum of hydrazine  $N_2H_4$  in the solid, liquid, and gaseous states a great number of projects (1, 2, 3, 4, 5, 6) have been devoted. In a number of the studies (5, 6, 7) attempts have been made at relating the frequencies of the molecule  $N_2H_4$  for the point group  $C_2$ , but in the project (8) a computation was made of the normal vibrations of a molecule of hydrazine  $N_2H_4$  by using the power invariables from the data for the molecules of methylamine  $CH_3NH_2$  and ammonia  $NH_3$  for the configuration with the angle of turn  $\theta$  of one group  $NH_2$  equal to  $90^\circ$ .

But since in recent time there have appeared new, more precise electronographic and spectroscopic data on the structure of the molecule of hydrazine (9, 10), it serves to end sought to repeat the computation of the vibration spectrum of the molecule of hydrazine. And in connection with the question of the rotational isomer of hydrazine some interest is afforded by the computation of the vibrational frequencies of the molecule

of hydrazine for different angles  $\theta$ .

We made a computation of the vibrational frequency of a molecule of hydrazine for the angles of turn  $\theta = 0^\circ, 60, 90, 120, \text{ and } 180^\circ$ . Below the results obtained are elucidated.

The expression for the potential energy of the molecule  $\text{N}_2\text{H}_4$  used in the computation can be presented in the form

$$\begin{aligned} 2V = & K_Q \cdot Q^2 + K_q \sum_i q_i^2 + K_\alpha \sum_{i \neq j} \alpha_{ij}^2 + \\ & + K_\beta \sum_i \beta_i^2 + 2K_{Q\beta} \sum_i Q\beta_i + 2K_{qq} \sum_{\substack{i,j=1,2 \\ i,j=3,4}} q_i q_j + \\ & + 2K_{q\alpha} \sum_{i \neq j} q_i \alpha_{ij} + 2K_{q\beta} \sum_i q_i \beta_i + 2K_{\alpha\beta} \sum_{i \neq j} \beta_i \alpha_{ij} + \\ & + 2K_{\beta\beta} \sum_{\substack{i,j=1,2 \\ i,j=3,4}} \beta_i \beta_j + 2K'_{\beta\beta} (\gamma_{\beta_i \beta_j}) \sum_{\substack{i,j=1,3,4 \\ i,j=2,3,4}} \beta_i \beta_j, \end{aligned}$$

where

$$K_Q, K_q, K_\alpha, K_\beta, K_{Q\beta}, K_{qq}, K_{q\alpha}, K_{q\beta}, \\ K_{\alpha\beta}, K_{\beta\beta} \text{ и } K'_{\beta\beta} (\gamma_{\beta_i \beta_j}) -$$

are the power invariables.  $\gamma_{\beta_i \beta_j}$  is the angle between the planes in which lie the angles  $\beta_i$  and  $\beta_j$ . The coordinates of the change of the internuclear distances  $Q_i, q_i$  and the valance angles  $\alpha_{ij}$  and  $\beta_i$  are given in the drawing.

The power invariables used in the computation had the following values (in  $10^6 \text{ cm}^{-2}$ ):  $K_Q = 8.11$ ;  $K_q = 10.36$ ;  $K_\alpha = 0.79$ ;  $K_\beta = 1.14$ ;  $K_{Q\beta} = 0.45$ ;  $K_{qq} = 0.05$ ;  $K_{q\alpha} = 0.35$ ;  $K_{q\beta} = 0.50$ ;  $K_{\alpha\beta} = K_{\beta\beta} = 0.035$ . These values of power invariables were borrowed from the data for the molecules  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{C}_2\text{H}_6$  (12). The value of the invariable  $K_Q$  was taken from the work (8). The

The invariables  $K_q$  and  $K_\beta$  were refined from the preliminary computation of the frequency of the molecule  $N_2H_4$ . The power invariable  $K'\beta\beta (\gamma\beta_i \beta_j)$  was roughly evaluated by the formula:

$$K'_{\beta\beta}(\gamma\beta_i \beta_j) = -0.12 + \frac{0.24}{180^\circ} \gamma\beta_i \beta_j.$$

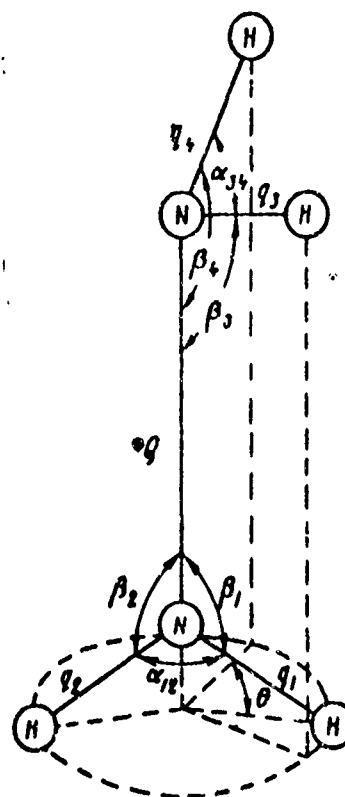
In determining the coefficients of the kinetic energy there were used the following geometrical parameters (9, 10);  $R(N--N) = 1.449 \text{ \AA}$ ;  $r(N--H) = 1.022 \text{ \AA}$ ;  $\alpha(HNH) = 106^\circ$  and  $\beta(NHH) = 112^\circ$ . The solution of the secular equations was done on the electronic computer Strela. The values for the frequencies of the molecule  $N_2H_4$  were calculated for the values  $\theta = 0^\circ$ ,  $60^\circ$ ,  $90^\circ$ ,  $120^\circ$ , and  $180^\circ$ .

The results of the computation are given in the table\*. In the last column for comparison there are given the experimental values of the frequencies borrowed from the work (6).

### Discussion of the Results

The computed values of the frequencies for  $\theta = 90^\circ$  are found to be in agreement with the results of the computation given in the report (8) for the configuration with  $\theta = 90^\circ$ .

As is seen from the table the course of the frequencies  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_5$ ,  $\nu_8$ ,  $\nu_9$  and  $\nu_{10}$  in the measurement of  $\theta$



\*For  $\theta = 0^\circ = 180^\circ$  the computation of the frequency was done both in accordance with the matrices of the types of symmetry A and B and in accordance with the matrices of the types of symmetry  $A_1, B_1$ , and  $A_g, B_g, A_u, B_u$ . Therefore in the table in the columns with  $\theta = 0^\circ$  and  $180^\circ$  after each frequency in the brackets there are shown types of symmetry of frequencies referring to the point groups  $C_{2v}$  and  $C_{2h}$ .

from  $0^\circ$  to  $180^\circ$  proves to be insignificant (at the maximum it reaches the value  $\sim 30 \text{ cm}^{-1}$ ). Therefore in accordance with the course of the change of these frequencies it is not possible to judge of the angle of turn  $\theta$  of one group  $\text{NH}_2$  relative to another group  $\text{NH}_2$ .

The frequencies  $\nu_4$  and  $\nu_{11}$ , on the other hand, change almost by  $350 \text{ cm}^{-1}$  in the transition from  $\theta = 0^\circ$  to  $\theta = 180^\circ$ . For the configuration with  $\theta = 90^\circ$  they have practically one and the same value equal to  $1270 \text{ cm}^{-1}$ . In the infrared spectrum of the absorption of the vapors of  $\text{N}_2\text{H}_4$  in this area there was noted one frequency. In accordance with the report (6) its value is equal to  $1275 \text{ cm}^{-1}$ , in accordance with (5)  $1282 \text{ cm}^{-1}$ . Such an agreement of experiment and computation clearly confirms the deduction made earlier in the projects (10, 11) that the most probable angle of turn  $\theta$  of the one group  $\text{NH}_2$  relative to another group  $\text{NH}_2$  is the angle  $\theta = 90^\circ$ .

The change in the frequencies  $\nu_6$  and  $\nu_{12}$  is also significant (it reaches  $\sim 150 \text{ cm}^{-1}$ ). The calculated values of the frequencies  $\nu_6$  and  $\nu_{12}$  for  $\theta = 90^\circ$  are respectively equal to 831 and  $859 \text{ cm}^{-1}$ . In the work (5) in the infrared spectrum of the absorption of the vapors of  $\text{N}_2\text{H}_4$  in this area there were revealed two weak bands 815 and  $850 \text{ cm}^{-1}$  and two strong bands 930 and  $965 \text{ cm}^{-1}$ . In a later work (6) in the infrared spectrum of the absorption of vapors of  $\text{N}_2\text{H}_4$  there were noted three strong bands 780, 933, and  $966 \text{ cm}^{-1}$ . As is seen from the comparison with the data of the table all these experimental values can be sufficiently well explained if one allows the existence of all three isomeric forms: the cis-forms ( $\theta = 0^\circ$ ), the trans-forms ( $\theta = 180^\circ$ ),

and the  $C_2$ -forms with  $\theta = 90^\circ$ . However, such an explanation results in objections for a number of other considerations. But, if one does not take into consideration the frequencies  $815$  and  $850 \text{ cm}^{-1}$ , taking into account that they were not repeated in the work (6), then one can satisfactorily explain the noted frequencies having taken the existence of only on " $C_2$ -form" with  $\theta = 90^\circ$ , as was done in the work (8). But the strong divergence of the computed and the experimentally determined values of the frequencies  $\nu_6$  and  $\nu_{12}$  in this case can be referred to imprecision of the respective power invariables.

For the solution of the problem of the correctness of any of these explanations very important is the investigation of the vibrational spectrum of the vapors of  $N_2D_4$  and the carrying out of a more precise computation.

Vibrational Frequency (in  $\text{cm}^{-1}$ ) of a Molecule of  $N_2H_4$  for Different Values of the Angle  $\theta$

Vibrations	Symmetry	$\theta = 0^\circ$	$\theta = 60^\circ$	$\theta = 90^\circ$	$\theta = 120^\circ$	$\theta = 180^\circ$	$\nu_{\text{exp}} [6]$
$\nu_1$	A	3317 ( $A_1$ )	3315	3313	3311	3310 ( $A_g$ )	3314
$\nu_2$		3345 ( $A_2$ )	3350	3355	3360	3364 ( $A_u$ )	3325
$\nu_3$		1613 ( $A_1$ )	1632	1628	1624	1641 ( $A_g$ )	1587
$\nu_4$		1419 ( $A_2$ )	1347	1270	1186	1070 ( $A_u$ )	1275
$\nu_5$		1043 ( $A_1$ )	1044	1044	1045	1052 ( $A_g$ )	1098
$\nu_6$		784 ( $A_1$ )	816	831	852	925 ( $A_g$ )	780
$\nu_7$	B	3305 ( $B_1$ )	3307	3309	3311	3313 ( $B_u$ )	3280
$\nu_8$		3364 ( $B_2$ )	3359	3355	3350	3345 ( $B_g$ )	3350
$\nu_{10}$		1669 ( $B_1$ )	1652	1656	1659	1638 ( $B_u$ )	1628
$\nu_{11}$		1071 ( $B_2$ )	1186	1269	1347	1419 ( $B_g$ )	1275
$\nu_{12}$		957 ( $B_1$ )	881	859	844	814 ( $B_u$ )	966
							933

#### Literature

1. S. Imanishi. Nature, 127, 782, 1931.



2. L. Kahovec and K. W. F. Kohlrausch. Z. Phys. Chem. (Journal for Physical Chemistry), Vol. 38, 96, 1938.
3. J. Goubeau. Z. Phys. Chem. (see foregoing Ref.), Vol. 45, 237, 1940.
4. S. S. Krivich. DAN SSSR, 23, 36, 1939.
5. W. Fresenius and J. Karwell. Z. Phys. Chem., Vol. 44, 1, 1939.
6. P. A. Giguere and I. D. Liu. J. Chem. Phys., 20, 136, 1952.
7. D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard, and H. M. Huffman. J. Amer. Chem. Soc., 71, 2293, 1949.
8. A. Yamaguchi. J. Chem. Soc. Japan, 80, 1109, 1959.
9. Y. Morino, T. Iijima, and Y. Murata. Bull. Chem. Soc. Japan, 33, 16, 1960.
10. A. Yamaguchi, I. Ichishima, T. Shimanouchi, and I. Mizushima. J. Chem. Phys., 31, 843, 1959; Spectrochim acta, 16, 1471, 1960.
11. W. G. Penney and G. B. B. M. Sutherland. J. Chem. Phys., 2, 492, 1934, Trans, Faraday Soc., 30, 898, 1934.
12. M. V. Vol'keishteyn, M. A. Yel'yashevich, B. I. Stepanov. Kolebaniya Molekul, Vol. 1, Gostekhzdat, M., 1949.